change of the shape with environmental conditions can be detected by the extinction angle change.

On the other hand, information on the optical anisotropy of solute particles obtained by flow birefringence is mostly qualitative. The theoretical foundation is not sufficient, however, for quantitative analyses.

Finally, it must be emphasized again that the usefulness of flow birefringence measurements is very much increased by combination with various other experimental methods.

3776

## [14] Electric Birefringence

*By* LEO D. KAHN

The suspended particles of a colloidal system, because of their dipolar nature, are oriented to an aligned state by an applied electric field to form an optically birefringent system that is essentially a uniaxial crystal. The electric birefringence technique takes advantage of this effect to study the characteristics of macromolecular suspensions as they respond to an electric field that is usually in the form of a square-wave pulse. In this way, it is possible to measure two characteristic electric birefringence constants, rotatory diffusion constant, permanent and induced dipole moments, electric polarizability, and optical anisotropy, as well as to determine whether a given macromolecular suspension is monodisperse. It is conceivable that by extending the techniques described here, electric birefringence should also prove useful in investigating the distribution of polymeric species in a suspension, aggregation phenomena, charge patterns of macromolecules, and particle–particle interaction.

A schematic diagram of the apparatus used is shown in Fig. 1. The optical train consists of a light source, monochromatic filter, two polarizing prisms (such as Rochon or Nicol prisms), and a photomultiplier aligned along an optical bench. The sample under investigation is held in a transparent optical cell positioned between the polarizing prisms, and two flat platinum electrodes are immersed in it so that the light beam passes between them. The amplified output of a square-wave generator is applied to the electrodes, and a dual-trace oscilloscope is used to display simultaneously the applied pulse and the optical response of the system.

The polarizing prisms are normally in the crossed position and in the quiescent state no light passes to the photomultiplier. When a square-

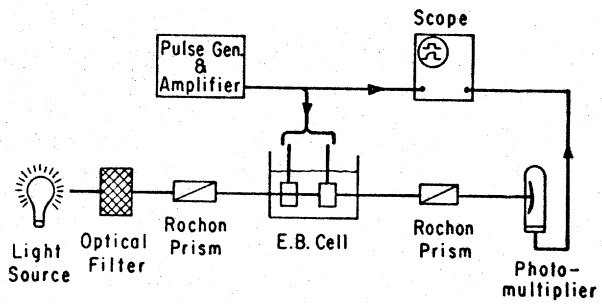


FIG. 1. Electric birefringence apparatus. From L. D. Kahn and L. P. Witnauer, *J. Amer. Leather Chem. Ass.* **64**, 12 (1969).

wave pulse is applied to the electrodes, the suspended particles rotate toward a state of alignment with the electric field and light reaches the photomultiplier. Its intensity will follow the mode of rotation of the suspended particles, which will, in turn, depend upon their size and shape, their permanent and induced dipole moments and frictional effects. The process is illustrated by the typical electric birefringence oscilloscope pattern shown in Fig. 2, where the square-wave trace depicts the electric field and the accompanying curved trace shows the optical response of the system. The leading edge of the applied pulse is followed

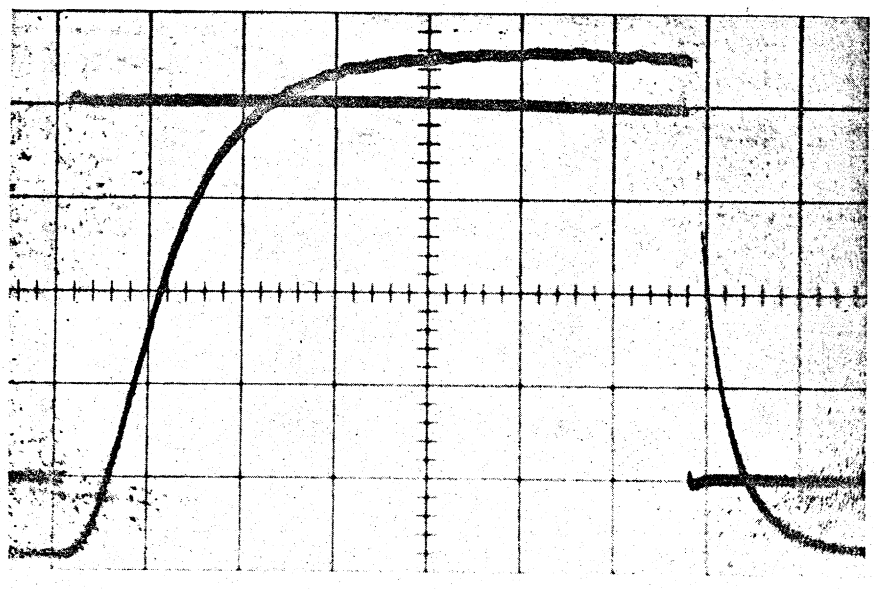

FIG. 2. Typical electric birefringence pattern.

almost immediately by a rapid buildup of birefringence which reaches a steady saturated state. When the applied pulse is terminated, there is an exponential decay of light intensity at the photomultiplier as the suspended particles return to a random orientation pattern through Brownian motion.

The birefringence of a macromolecular suspension in an electric field is defined as the difference between the indices of refraction parallel to the electric field and perpendicular to it, and is represented by $\Delta n$ which can be either positive or negative. It can be expressed in either linear or angular terms through the relations[1]

$$\Delta n = \frac{\lambda\delta}{l} = \frac{\lambda\phi}{2\pi l} \tag{1}$$

where $\lambda$ is the wavelength of the light, $\delta$ is the linear phase difference between corresponding points on the ordinary and extraordinary light waves, $l$ is the length of the light path between the electrodes, and $\phi$ is the phase angle corresponding to $l$. It is convenient to measure electric birefringence in degrees of angle as given via the calibration procedure to be described below in the section on experimental procedure.

Reviews of the theoretical basis of electric birefringence and development of the mathematical relations involved have been published by Benoit,[1] Peterlin and Stuart,[2] O'Konski *et al.*,[3] Tinoco,[4] O'Konski,[5] Yoshioka and Watanabe,[6] and Kahn.[7]

## Apparatus

Complete apparatus for electric birefringence measurements is not available on the market at the time of writing, and anyone who plans to enter this field of research must be prepared to design and construct the necessary optical train and much of the electronic circuitry.

### *Optical Train*

The optical components can be assembled on an optical bench, or an existing photoelectric polarimeter can be modified to serve the purpose as illustrated by the Rudolph Model 80 unit shown in Fig. 3.

[1] H. Benoit, *Ann. Phys.* **6**, 561 (1951).
[2] A. Peterlin and H. A. Stuart, *Z. Phys.* **112**, 129 (1939).
[3] C. T. O'Konski, K. Yoshioka, and W. H. Orttung, *J. Phys. Chem.* **63**, 1558 (1959).
[4] I. Tinoco, Jr., *J. Amer. Chem. Soc.* **77**, 4486 (1955).
[5] C. T. O'Konski, "Encyclopedia of Polymer Science and Technology," Vol. 9, p. 551. Wiley (Interscience), New York, 1968.
[6] K. Yoshioka and H. Watanabe, *in* "Physical Principles and Techniques of Protein Chemistry" (S. J. Leach), Part A, p. 335. Academic Press, New York, 1969.
[7] L. D. Kahn, *J. Food Agr. Chem.* **19**, 679 (1971).

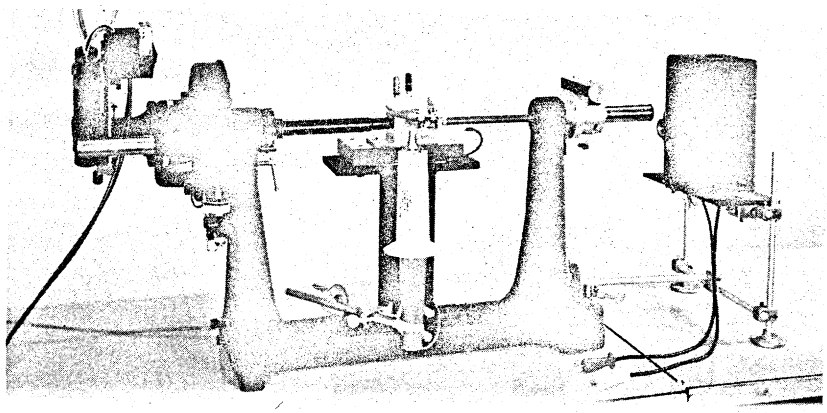

FIG. 3. Rudolph Model 80 polarimeter modified for use in electric birefringence measurements.

This instrument was already equipped with Rochon prisms and photomultiplier. Modification consisted principally of replacing the metal chamber that held the polarimeter tube by a holder for the electric birefringence cell and two light tunnels leading to it. Addition of a lamp house and filter turret plus a photographic shutter and removal of the prism oscillating motor completed the modification.

The plane of polarization is usually set at an angle of 45° with the electric field, and the polarizer prism to permanently positioned at this angle. The analyzer prism should be mounted on a calibrated circle so that it can be rotated through definite angles relative to the polarizer for purposes of standardization.

Illumination should come from an incandescent lamp rather than an arc or discharge lamp, so as to keep noise to a minimum. A 100-W projection lamp powered by a dc power supply will usually provide sufficient illumination. However, because sensitivity of the apparatus increases with light intensity, it may be desirable to use a 250-W marine searchlight or locomotive headlight lamp. It is possible to achieve brighter illumination by operating the incandescent lamp above its rated current, but this reduces its life-span to a considerable degree. Further refinement of the optical system can be introduced by adding lenses to collimate the light beam. The lamp power supply must have a current control that varies output smoothly and continuously over its entire range, and its regulating system should be programmed for constant current. A photographic shutter in the light path is necessary so that the light can be cut off to establish a base line on the oscilloscope screen.

*The Cell*

A practical electric birefringence cell for use with macromolecular suspensions follows the design of O'Konski and Haltner.[8] One version of this is shown in Fig. 4. The envelope is a standard 1 cm² cross section spectrophotometer cell. The two limbs which carry the platinum sheet electrodes are made of glass, and their end projections normal to the light beam are painted black to eliminate light leakage. The top of the cell is made of a block of Plexiglas and bears two pins that fit into mating holes in the cell holder so that positioning will be reproducible. The cell holder seen in Fig. 3 can be constructed of sheet brass and water jacketed if desired. The two clip leads which attach to the high voltage terminals should be as short as possible, preferably less than 10 cm long, so as to reduce stray capacitance. Also, the termination of the cable leading from the pulse amplifier and the high voltage probe for the oscilloscope should be located close to the cell holder.

*Pulse Generator and Amplifier*

The pulse generator used in electric birefringence measurements should have a high amplitude output (50 V is usual) in order to minimize the gain required of the amplifier.

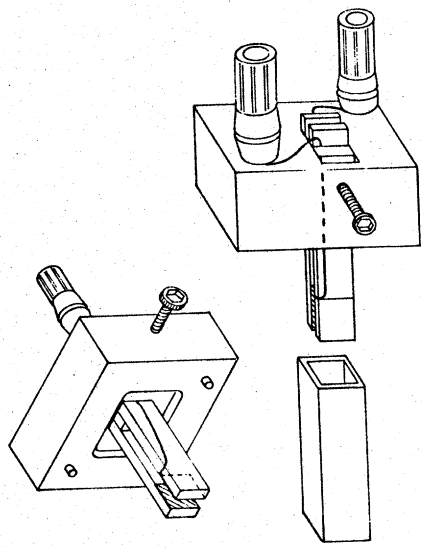

FIG. 4. Electric birefringence cell.

[8] C. T. O'Konski and A. J. Haltner, *J. Amer. Chem. Soc.* **78**, 3604 (1956).

The pulse amplifier will generally have to be designed and built to suit an anticipated research program. In addition to sufficient gain, it must preserve pulse shape over the range of pulse widths and amplitudes required by the proposed research. This requires that adequate high frequency, low frequency, and phase shift compensation be incorporated.

The wiring diagram of an amplifier used in research on dissolved collagen is shown in Fig. 5 and, while it has a relatively low pulse output amplitude suitable only for colloidal particles having a very large overall dipole moment, it illustrates many of the points that must be considered when designing an amplifier for electric birefringence service. This amplifier consists of a single stage plus cathode follower and preserves square-wave shape for pulses up to 20 msec in width. Low frequency and phase shift compensation are adjusted by varying the load the cathode follower imposes on the amplifier tube. This is accomplished by adjusting the filament current of the cathode follower tube via the Variac. This is set to the proper value prior to an actual run by selecting the Variac setting that gives good pulse reproduction. In this particular amplifier it was found that floating the coupling condenser between the stages, i.e., leaving its container ungrounded, made high frequency compensation unnecessary. The Amphenol connector at the output mates with the line to the electric birefringence cell which is the load for the cathode follower. The dc power supply in the grid circuit of the cathode follower

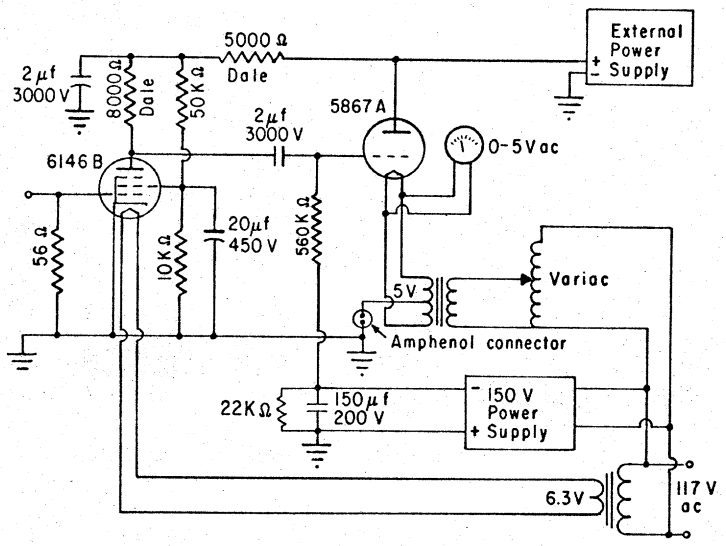


FIG. 5. Pulse amplifier for use in electric birefringence.

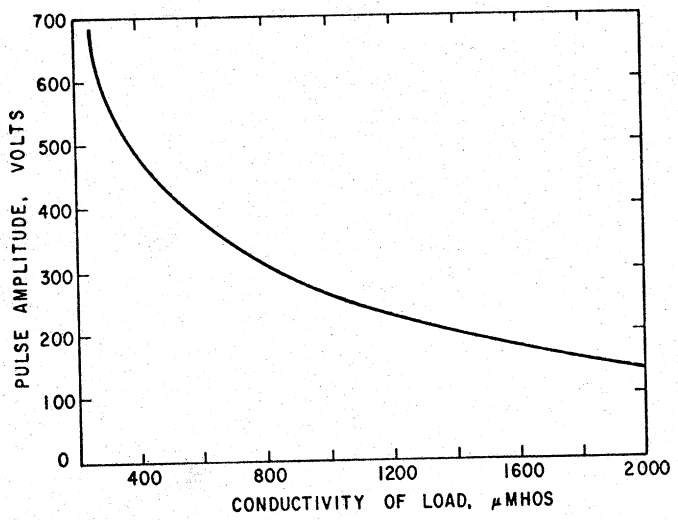


FIG. 6. Load characteristic of pulse amplifier.

biases it to cutoff and thus clamps the output pulse to ground potential. The use of a cathode follower is essential if the oscilloscope is to display the pulse across the electric birefringence cell, rather than the pulse across the output of the amplifier tube. It is also a valuable safety feature when loading or manipulating the cell, because in this case there is no electric potential across the cell when a pulse train is not active.

The load characteristic of the amplifier illustrated with the high voltage supply set at 2400 V is drawn in Fig. 6, which shows that the amplitude of the output pulse is limited by the conductivity of the electric birefringence cell. The high voltage power supply for an electric birefringence amplifier must be well regulated, and the magnitude of its ripple must be taken into consideration. When pulses of very high amplitude or power are needed, it will be necessary to use a pulse generator employing thyratrons.

*Oscilloscope and Photomultiplier Circuit*

To minimize heating, electrophoresis, and electrolysis of the sample in investigations of electric birefringence, it is customary to use either single pulses or short bursts of pulses, rather than long pulse trains of indefinite duration. For this reason the oscilloscope used must have a data storage system, so that an electric birefringence pattern can be held on the screen until no longer wanted.

The signal-to-noise ratio can be improved by increasing the intensity of the light and reducing the polarizing potential across the photomulti-

plier. Further reduction in noise can be achieved by using a refrigerated photomultiplier housing cooled by Dry Ice.

In most cases, high frequency compensation will have to be incorporated in the photomultiplier circuit. This can usually be accomplished by means of a simple integrating circuit between the photomultiplier and oscilloscope. The fidelity of the photomultiplier circuit can be verified by passing a square-wave light pulse generated by an avalanche diode. A Fairchild FLB-100 diode connected to an EH Laboratories Model 132A-8 pulse generator will produce enough light at a potential 7 V to excite a 1P21 photomultiplier. The light pulse created by this diode has rise and decay times of less than 10 nsec.

Since the buildup and decay phases of the electric birefringence pattern yield different types of information, it is convenient to display either one alone with the sweep speed set so that the pattern will just fill the oscilloscope screen. This can be done by using delayed trigger pulses supplied by either the pulse generator or the oscilloscope to control the time of initiation of the pulse and of the oscilloscope sweep relative to each other. If a burst of square waves is to be used to give a pattern of electric birefringence curves superimposed on each other, a sequence of delay generators to trigger functions in the proper order must be set up.

To give an estimate of the capability of a typical apparatus, we consider the following arrangement: The optical system employs a 100-W General Electric projection lamp type CPG used without an optical filter and the light beam is reduced by the electric birefringence cell to a rectangular cross section of 3 mm by 6 mm; the electrical side uses a 1P21 photomultiplier polarized by 500 V. When this was used to study the electric birefringence of dissolved collagen preparations, measurements over the range of 0.01 to 48.0 degrees of angle could be made to a reproducibility of better than $\pm 2\%$. Measurements could be made at smaller angles, but the accuracy of measurement decreased progressively and reached a reproducibility of $\pm 20\%$ at an electric birefringence of 0.001 degree of angle.

## Experimental Procedure

To compensate for the depolarization and light absorbance of the sample, and thus relate all measurements in a sequence to the same base line, the intensity of the light source must be adjusted prior to each measurement in the following way. First, the analyzer prism is rotated from its crossed position through an angle whose value is somewhere in the middle of the range of birefringence values anticipated so that light passes through the system. This is now the standard angle for the run

and also for the calibration. The oscilloscope gain and light intensity are then adjusted to give a definite deflection of the oscilloscope beam, which will be known as the standard deflection. This is best observed by using dc input to the oscilloscope, setting a slow sweep rate, and snapping the shutter at an exposure setting of about 0.5 sec. Uniformity is achieved by carrying out this procedure, adjusting to the same standard deflection at the same standard angle for each sample. The analyzer prism is then returned to the crossed position prior to application of the electric field.

Calibration is best carried out by a modification of Benoit's procedure.[1] After standard conditions are established, as described in the previous paragraph, oscilloscope deflections are observed in the same way with the prisms crossed and with the analyzer set to a number of angular intervals to give a series of calibration points. By following this procedure, the light chopper used by Benoit is not required. Each value of deflection is adjusted by subtracting the deflection at the crossed position of the prisms and a calibration curve of adjusted oscilloscope deflection versus the angular deviation of the analyzer from the crossed position is drawn. This calibration curve is valid for all observations made at its particular standard angle and standard oscilloscope deflection. To cover a wide range of birefringence measurements, it may be necessary to prepare several calibration curves corresponding to different values of standard angle. Because of the variable spectral response characteristic of a photomultiplier, the calibration curve and the electric birefringence measurements should be carried out at the same wavelength of light.

It is advisable to use a fresh portion of sample for each observation unless it is definitely known that the electric field does not alter the macromolecular preparation. In carrying out preliminary observations to verify the shape of the applied pulse before an actual birefringence measurement, the sample can be conserved by substituting a dummy load. This is a variable noninductive resistance whose value has been set to that of the filled cell.

If the wavelength of the light is not restricted by the nature of the experiment being carried out, the direct illumination of the lamp without a filter can be used to obtain greater light intensity. Its average wavelength can be determined by running identical samples with a series of filters covering the visible range and noting which one gives the same response as the white light.

A convenient rate of oscilloscope sweep for displaying the decay portion of the electric birefringence curve will often be too rapid to locate the zero datum line. This can be remedied by superimposing on

the decay trace retained on the oscilloscope screen a second decay trace obtained with the same sample at a sweep rate so much slower that most of its length will be at the zero birefringence level.

## Calculations

It has been observed that electrically birefringent systems show a linear relation between birefringence and the square of the electric field strength at low values of the latter. This is the Kerr law and the region over which it is valid is the Kerr region.[9] This leads to two characteristic Kerr constants of an electrically birefringent system, $B$ and $K$ defined as follows[9,10]

$$B = \frac{\Delta n}{\lambda E^2} = \frac{\phi}{2\pi l E^2} \tag{2}$$

$$K = \frac{\Delta n}{n E^2} \tag{3}$$

where $E$ is field strength in volts and $n$ is the index of refraction of the macromolecular suspension when no electric field is present. The value of $l$, the length of the light path between the electrodes can be corrected for electrode end effects by the formula of Chaumont.[11]

$$l = l_0 + \frac{a}{\pi}\left[1 + \frac{d}{a}\ln\left(1 + \frac{a}{d}\right)\right] \tag{4}$$

where $l_0$ is the measured length of the electrodes, $a$ is the gap between them, and $d$ is their thickness. Either Kerr constant can be obtained from the slope of a graph of $\Delta n$ versus $E^2$ in the Kerr region. Specific constants can be determined by dividing $B$ or $K$ by the concentration of the sample.

A technique for determining permanent and induced dipole moments as well as the polarizability of macromolecules in suspension from the electric birefringence at the saturation phase of the buildup curve has been developed by Yoshioka and Watanabe[6] and also by Yamaoka.[12] This method is based on a mathematical analysis of the electric birefringence of a macromolecular suspension by O'Konski *et al.*,[3] which is developed as follows:

The electric field creates a definite angular distribution of the suspended particles which can be expressed in terms of a function, $f(\theta,t)$ where $\theta$ is the angle between the principal hydrodynamic axis

[9] J. Kerr, *Phil. Mag.* [4] **50**, 337, 446 (1875); [5] **9**, 157 (1880).
[10] P. Debye, *in* "Handbuch der Radiologie," Vol. 6, 597. Akad. Verlagsges, Leipzig, 1925.
[11] L. Chaumont, *Ann. Phys.* **5**, 31 (1916).
[12] K. Yamaoka, Ph.D. Thesis, Univ. of California at Berkeley, 1964.

of a particle and the electric field, and $t$ is the buildup time. The birefringence of a macromolecular suspension is a function of particle orientation which can be expressed by an orientation factor, $\Phi$, which is related to $\theta$ via

$$\Phi = \tfrac{1}{2}\,(3 < \cos^2\theta > - 1) \tag{5}$$

The permanent dipole moment and the electric polarizability can be put in terms of $\theta$ by means of energy considerations combined with the Boltzmann distribution law, and then related to $\Phi$ through two dimensionless quantities, $\beta$ and $\gamma$, defined by

$$\beta = \frac{\mu E}{kT} \tag{6}$$

$$\gamma = \frac{(\alpha_1 - \alpha_2)\,E^2}{2kT} \tag{7}$$

where $\mu$ is the permanent dipole moment, $k$ is the Boltzmann constant, $T$ is temperature, and $\alpha_1$, $\alpha_2$ are the excess polarizabilities of the suspended macromolecular particles over the solvent in directions parallel to and perpendicular to their principal hydrodynamic axis. This leads to the equations

$$\frac{15\Phi(\beta,\gamma)}{\beta^2 + 2\gamma} = \frac{\dfrac{\Delta n}{E^2}}{\left(\dfrac{\Delta n}{E^2}\right)_{E\to 0}} \tag{8}$$

and

$$15\Phi(\beta,\gamma) = (\beta^2 + 2\gamma)_{E\to 0} \tag{9}$$

These relate the measurable values, $\Delta n$ and $E^2$ to the parameters of the theoretical equations and can be made numerically identical graphically by properly adjusting the scales of the dimensionless terms. This is done by plotting a family of curves of values of $[15\phi(\beta,\gamma)]/(\beta^2 + 2\gamma)$ as ordinates, and values of ln $(\beta^2 + 2\gamma)$ as abscissas for a series of values of $\beta^2/2\gamma$. These should include in addition to curves for $\beta^2 = 0$ and $\gamma = 0$, those covering the range up to $\beta^2/2\gamma = 12$. There is little to be gained by extending this ratio beyond the latter value, because curves plotted to higher values will have very nearly the same contour, and this sets a limit to the useful range of this technique. Numerical values that can be used for plotting these data have been published by Matsumoto *et al.*[13] or values can be taken from the graph in Fig. 7, which

[13] M. Matsumoto, H. Watanabe, and K. Yoshioka, *Sci. Pap. Coll. Gen. Educ. Univ. Tokyo* **17**, 173 (1967).

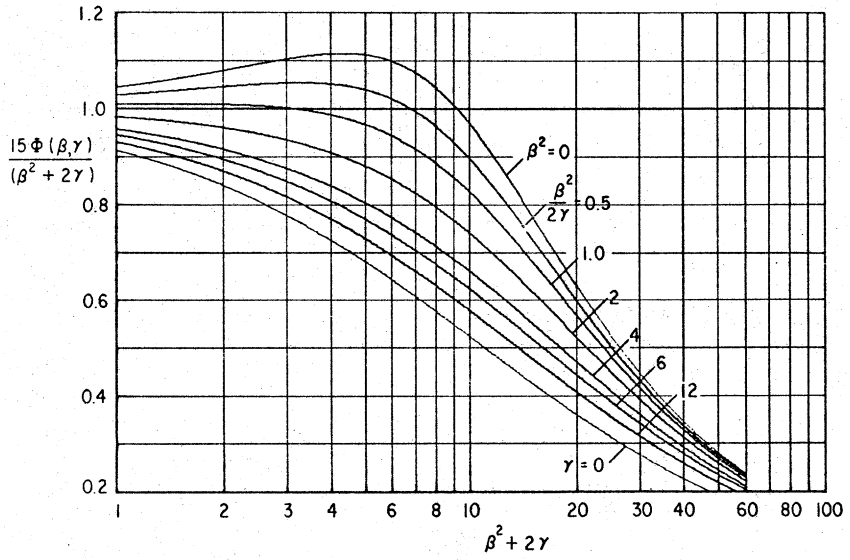


FIG. 7. Graph of theoretical electric birefringence relations for use in calculating permanent dipole moment and polarizability.

was drawn by digital computer from equations given by O'Konski *et al.*[3] As the next step, the experimental values of

$$\frac{\frac{\Delta n}{E^2}}{\left(\frac{\Delta n}{E^2}\right)_{E\to 0}}$$

are plotted versus ln $E^2$ on transparent paper using the same scales as in the previous curves. The latter graph is then superimposed on the family of theoretical curves, and the logarithmic scales are moved relative to each other until the experimental points coincide with one of the theoretical curves. The numerical values of $\beta$ and $\gamma$ for the run are now available, and Eqs. (6) and (7) can be solved to yield values of permanent dipole moment and polarizability. The induced dipole moment, $\Psi$, is then obtained from

$$\Psi = (\alpha_1 - \alpha_2)\, E \tag{10}$$

Examples of this type of calculation are given by Yamaoka[12] and by Kahn.[7] The entire calculation, including the matching of the graphs, can be carried out on a digital computer having a capability equal to the IBM Model 1130.

The relation between the optical anisotropy and the electric bire-

fringence of a macromolecular suspension has been given by Peterlin and Stuart[2] as

$$\Delta n = \frac{2\pi C_v(g_1 - g_2)}{n} \Phi \tag{11}$$

where $C_v$ is the volume fraction of solute and $(g_1 - g_2)$ is the optical anisotropy factor of the suspended particles.

Since $\Phi \to 1$ as $E \to \infty$ this can be used to determine the optical anisotropy factor by extrapolating a graph of $\Delta n$ versus $1/E^2$ to $1/E^2 = 0$, and then substituting the limiting value of $\Delta n$ in the following equations.[6]

$$\Delta n = \frac{2\pi C_v(g_1 - g_2)}{n} \quad \text{for } (\alpha_1 - \alpha_2) > 0 \tag{12}$$

$$\Delta n = \frac{\pi C_v(g_1 - g_2)}{n} \quad \text{for } (\alpha_1 - \alpha_2) < 0 \tag{13}$$

All points on the electric birefringence buildup curve of suspended particles, at low values of field, are related to the permanent and induced dipole moments through Benoit's equation[1]

$$\frac{\Delta n}{\Delta n_\infty} = 1 - \frac{3r}{2(r+1)} e^{-2Dt} + \frac{r-2}{2(r+1)} e^{-6Dt} \tag{14}$$

where $\Delta n_\infty$ is the birefringence at saturation, $D$ is the rotatory diffusion constant of the suspended macromolecules which can be determined from the electric birefringence decay curve, $t$ is buildup time, and

$$r = \frac{P}{Q}$$

with

$$P = \frac{\mu^2}{k^2T^2}$$

and

$$Q = \frac{(\alpha_1 - \alpha_2)}{kT}$$

Equation (14) was derived by expressing the angular distribution of suspended particles as a series of Legendre polynomials and inserting this in the diffusion equation. It can be seen from these relations that $r$ expresses the ratio of permanent to induced dipole moment. When it is positive, the permanent and induced dipole moments are in the same direction; and when it is negative, they are opposed.

The decay phase of the electric birefringence curve yields a test for monodispersity, a way of measuring rotatory diffusion constant, and a

means of studying polydispersity. The birefringence of a monodisperse preparation at any point on the decay curve is given by Benoit[1] as

$$\Delta n = \Delta n_0 e^{-6Dt} \tag{15}$$

where $\Delta n_0$ is the birefringence at the instant the square wave pulse is quenched, and $t$ is the decay time as measured from that point. If the macromolecular preparation under observation is monodisperse, a graph of ln $(\Delta n/\Delta n_0)$ versus $t$ will be a straight line with a negative slope of $6D$. The rotatory diffusion constant is related to the dimensions of an ellipsoid of revolution by Perrin's equation,[1,14] which can be simplified where the difference in axial lengths is large to[15]

$$D = \frac{3kT}{16\pi\eta a^3}\left(2\ln\frac{2a}{b} - 1\right) \quad \text{for } a > b$$

$$D = \frac{3kT}{32\eta a^3} \quad \text{for } a < b$$

where $\eta$ is the viscosity of the dispersion medium, $a$ is the length of the semiaxis of revolution of the suspended particles, and $b$ is the transverse semiaxis. The rotatory diffusion constant is related to the dimensions of a rod by Burgers' equation[16]

$$D = \frac{3kT}{8\pi\eta a^3}\left(\ln\frac{2a}{b} - 0.8\right)$$

If the preparation under study is polydisperse, each macromolecular species present will contribute a straight line component to the semilogarithmic decay graph, and the sum of these will appear as a curved line, thus giving a test of monodispersity.[1] It has been shown that resolving a composite curve of this type into more than two components is extremely difficult.[17] Studies of macromolecular suspensions by means of decay curves have been published by O'Konski and Haltner,[8] Ingram and Jerrard,[18] and Kahn and Witnauer.[19]

## Innovations

The optical system described is unable to discriminate between positive and negative birefringence. It can be made to do so by incorporating

[14] F. Perrin, *J. Phys. Radium* **5**, 497 (1934); **7**, 1 (1936).
[15] A. E. Alexander and P. Johnson, "Colloid Science," Vol. I, p. 386. Oxford Univ. Press, London and New York, 1949.
[16] J. M. Burgers, *Verh. Kon. Ned. Akad. Wetenschap., Afdel Natuurk., Sec. I*, **16** (4), 113 (1938).
[17] D. G. Gardner, J. C. Gardner, and W. W. Meinke, *J. Chem. Phys.* **31**, 978 (1959).
[18] P. Ingram and H. G. Jerrard, *Brit. J. Appl. Phys.* **14**, 572 (1963).
[19] L. D. Kahn and L. P. Witnauer, *J. Amer. Leather Chem. Ass.* **64**, 12 (1969).

a quarter-wave retardation plate between the birefringence cell and the analyzer.[5,6,20] The axis of the quarter-wave plate is in the same direction as the optical axis of the polarizer. The sensitivity of the system can now be increased by rotating the analyzer prism slightly from the crossed position. The optimum setting is given by

$$\sin \omega = \left(\frac{I_s}{I_0}\right)^{1/4}$$

where $\omega$ is the angular deviation from the crossed position, $I_s$ is the stray light intensity as measured with the polarizing prisms crossed, and $I_0$ is the light intensity transmitted with the optical axes of the prisms parallel. If this modification of the optical system is used, calibration will, of course, have to be carried out under the same conditions.

The electric birefringence technique is not limited to simple square-wave pulsed fields. Other shapes that have been used include alternating positive and negative square waves (reversed square wave) and alternating sine waves.[21-23]

**Acknowledgment**

The use of an avalanche diode to verify the fidelity of the photomultiplier circuit was suggested by Joseph A. Connelly. The family of curves in Fig. 7 was programmed and produced by a computer group consisting of Dr. C. Roland Eddy, Cecilia A. Finley, Brandt Kramer, and Ruth D. Zabarsky.

[20] C. T. O'Konski and B. H. Zimm, *Science* **111**, 113 (1950).
[21] M. Matsumoto, H. Watanabe, and K. Yoshioka, *J. Phys. Chem.* **74**, 2182 (1970).
[22] C. T. O'Konski and A. J. Haltner, *J. Amer. Chem. Soc.* **79**, 5634 (1957).
[23] I. Tinoco, Jr., and K. Yamaoka, *J. Phys. Chem.* **63**, 423 (1959).

## [15] Dielectric Dispersion Measurement of Dielectric Constant and Conductivity

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There are, roughly, two experimental methods for investigating the dielectric relaxation of polar molecules. One consists of measurements in the time domain, the other in the frequency domain. As will be explained later, these two measurements are essentially the same. In other words, the quantities measured by the former method can be converted into the quantities measured by the latter method and vice